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13. ABSTRACT (Maximum 200 words) This program addresses the extremely challenging problem of direct, in situ diagnostics of the heterogeneous surface reaction zone of energetic materials combustion. Specifically, the experiments employed an optical diagnostic, Raman scattering, to provide critically-needed species- and temperature-specific information on surface and near-surface reaction zones of modern, nitramine-based propellant formulations. Experiments employed a laboratory-scale, motorized, and servo-controlled, strand burner over a range of pressure from 1-20 atm. Broadband Raman scattering from the surface layer was acquired with a spectrograph detection system and Stokes/anti-Stokes ratios were used to provide surface temperature measurements. Raman thermometry was shown to be an effective diagnostic for surface temperature measurements of RDX combustion. The temperature sensitivity of the Raman spectrum of RDX was analytically modeled and verified by experimental data. The optical properties, reflectivity and absorptivity, were measured at 532 nm during this investigation. Signal interferences and laser perturbations (laser damage threshold, laser induced heating, laser induced fluorescence) were investigated at excitation wavelengths of 355, 532 and 683 nm. The surface temperature measured with Raman thermometry was in excellent agreement with the results of microthermocouple data obtained in other laboratories.					
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## SUMMARY

UTRC has undertaken an experimental program that addresses the extremely challenging problem of direct, in situ diagnostics of the heterogeneous surface reaction zone of energetic materials combustion. Specifically, the experiments employed an optical diagnostic, Raman scattering, to provide critically-needed species- and temperature-specific information on surface and near-surface reaction zones of modern, nitramine-based propellant formulations. A critical element of this program is the evaluation of interferences and perturbations that may impact the accuracy of measurements. Experiments employed a laboratory-scale, motorized, and servo-controlled, strand burner over a range of pressure from 1–20 atm. Broadband Raman scattering from the surface layer was acquired with a spectrograph detection system and Stokes/anti-Stokes ratios were used to provide surface temperature measurements.

The major results of this study are:

- The surface temperature of combusting RDX at 1 atmosphere was determined with Raman thermometry.
- Results from Raman thermometry agree very well with microthermocouple results from other laboratories.
- The Raman spectrum of RDX was calibrated over the temperature range of 22C to 128C and agreed well with theoretical predictions.
- Laser induced fluorescence contributes a large background signal to the Raman spectrum of RDX at combustion surface temperatures.
- The reflectivity and absorptivity of RDX were measured for 532 nm excitation.
- The threshold for laser damage at 532 nm was determined.
- Interference from temperature dependent fluorescence inhibits Raman thermometry of XM43 at elevated pressure when excited by 532 nm radiation.

## RESEARCH GOALS

The specific research goals of this contract were:

### Task I—Surface Diagnostics

UTRC shall apply Raman scattering diagnostics for the measurement of surface temperature during the combustion of nitramine based propellants. Attempts will be made to observe and identify the Raman signatures of condensed phase species.

## **Task II—Support of URI**

UTRC will provide temporary (*e.g.*, summer) employment for student staff of the Pennsylvania State University URI. This will provide an opportunity to learn state-of-the-art optical diagnostic techniques and an opportunity to learn the utility of and to compare data from complementary diagnostic techniques.

## **Task III—Integration of Results into Propellant Combustion Program**

UTRC shall evaluate the data obtained in Task I and compare it to predictions of combustion models and to data obtained by other researchers involved in the combustion of energetic materials. The nitramine combustion data will be supplied to modelers for refinement of combustion codes. UTRC will collaborate with the other participants in the propellant combustion community through the wide distribution of the results in formal and informal presentations and communications.

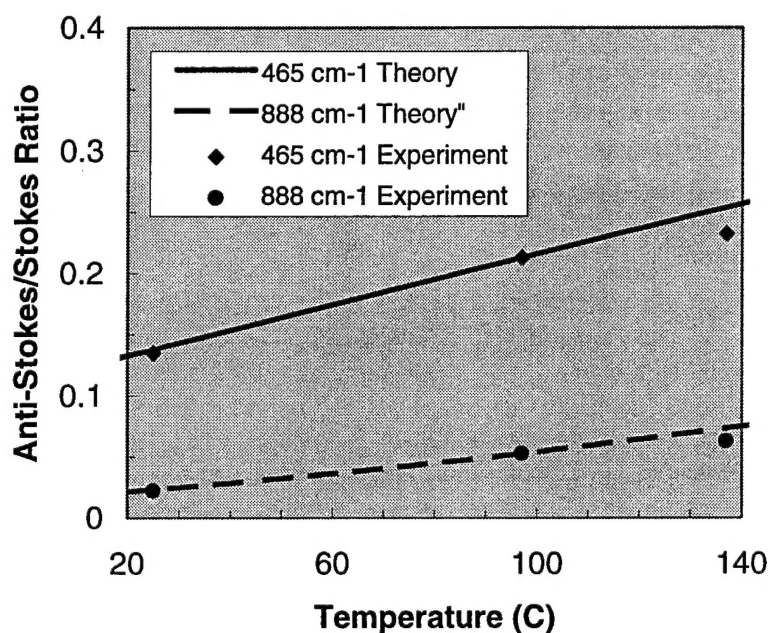
## **TECHNICAL ACCOMPLISHMENTS**

Task I: The first phase of the program investigated the Raman spectrum and optical properties of RDX. The laser damage threshold of RDX was investigated and the optical properties at 532 nm were measured. An analytical model of the temperature sensitivity and signal strength of the Raman spectrum of RDX was developed. Comparison of the signal strength prediction with experimental data was excellent. The results of this work were presented at the 32<sup>nd</sup> JANNAF Combustion Subcommittee Meeting and the paper is included in Appendix A of this report. The next phase of investigation was the temperature calibration of the Raman spectrum of RDX when excited at 532 nm. This work is reported in Appendix B, including the experimental arrangements used. The result of the initial temperature calibration was a discrepancy between the experimental results and the theoretical prediction of the temperature sensitivity of the Anti-Stokes to Stokes ratio for temperatures above 110C. It was felt the discrepancy may be due to interference of laser induced fluorescence at 532 nm and a decision was made to investigate alternate excitation wavelengths.

Raman spectra from 683 nm excitation. Spectrofluorimeter scans showed the room-temperature fluorescence would be less for excitation wavelengths greater than 650 nm. A system was designed for 683 nm excitation that employed a Raman cell filled with hydrogen and pumped by the 532 nm output of the Nd:YAG laser. A Raman Notch filter was purchased for rejection of 683 nm scattered light from the detected signal. Calculations based on the measured reduction of fluorescence at 683 nm and, taking into account the spectral sensitivities of the detector, spectrograph and Raman scattering cross section, indicated an increase in signal to interference of a factor of eight. The 683 nm configuration also used a 1/3-meter spectrograph which allowed both Stokes and anti-Stokes transitions to be acquired simultaneously which increases the confidence of Raman thermometry measurements. As in the experiments with 532 nm, a tungsten lamp was used to calibrate the gain of the system at 683 nm excitation. The temperature calibration data are limited to a surface temperature of approximately 140C by the experimental hardware. The RDX samples (~10 mm long) are heated from the bottom in the combustion



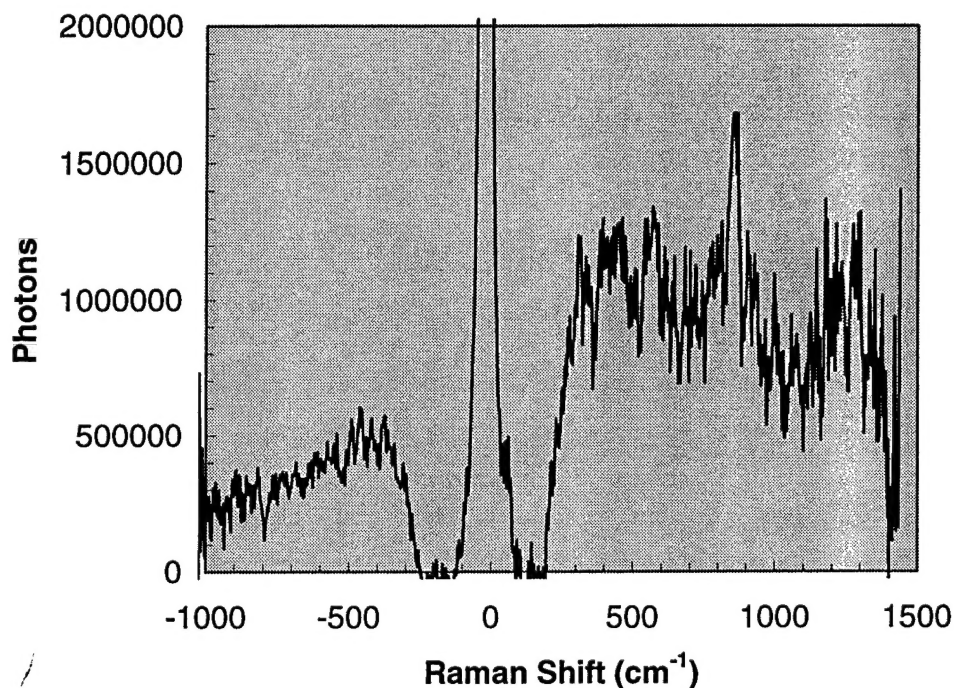
vessel. When the bottom temperature reaches 190C, heating is turned off to avoid melting the bottom of the sample. At this point the temperature of the top surface, monitored by a second thermocouple is ~137C. Raman spectra of heated RDX were acquired and transformed into the number of photons collected by means of the gain calibration. The spectra did demonstrate a higher signal to interference ratio than for excitation at 532 nm, however the sensitivity of the detection system was reduced, mainly due to the roll off of the OMA detector and the diffraction grating with increasing wavelength. The result was more shot noise in the spectra. An alternate, more local subtraction of the fluorescence background was also used for the 683 nm spectra. In the 532 nm case, the fluorescence was estimated as a linear function of wavelength over the range of the spectrum. This allowed efficient manipulation of the data in a spreadsheet to arrive at an anti-Stokes/Stokes mode intensity, however a localized estimate, in the vicinity of each mode, is deemed more precise. The Stokes and anti-Stokes mode intensities were extrapolated from the spectra and their ratio compared to theoretical prediction. The analytical model that predicts the temperature sensitivity of ratio is described in Stufflebeam, (1995) (Appendix A). The temperature calibration of the Raman spectrum of RDX, excited at 683 nm is shown in Figure 1. The agreement between experimental data and theoretical predictions of the anti-Stokes/Stokes ratio is excellent. The experimental data does not diverge from the prediction above 100C as was the case for 532 nm excitation (see appendix B).



**Figure 1.** Temperature calibration of two modes of the Raman spectrum of RDX, laser excitation at 683 nm.

Spectra from combusting RDX were acquired and a typical result is shown in Figure 2. The spectrum is an accumulation of 200 laser shots, or 20 seconds of burning. The accumulation time is restricted by the sample size, it is consumed in approximately 25 seconds at 1 atmosphere pressure. The feature at 0  $\text{cm}^{-1}$  shift is unrejected 683 nm scatter. The only other easily

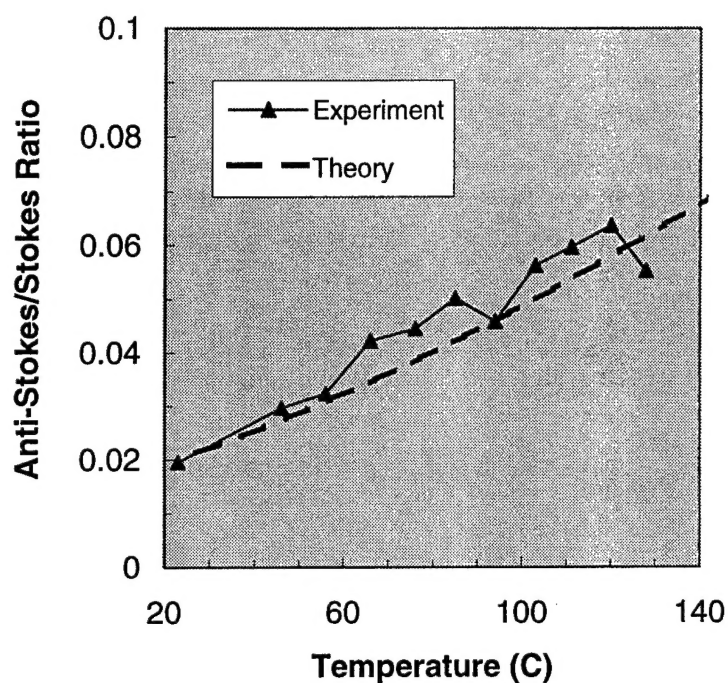
identified feature is the Stokes mode at  $888\text{ cm}^{-1}$ . The noise level in the spectrum prohibits an estimate of anti-Stokes/Stokes ratio for any mode and therefore the data is not usable for a temperature estimate. Resources did not permit acquisition of a detector and spectrograph optimized for sensitivity at  $683\text{ nm}$ , so a decision was made to attempt Raman thermometry at  $532\text{ nm}$  once more.



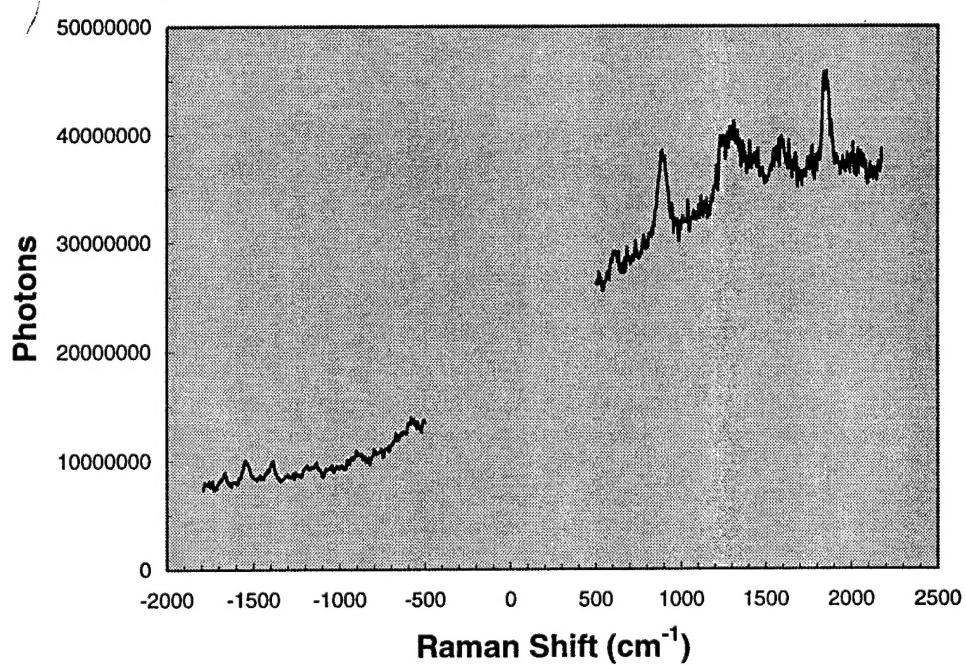
**Figure 2.** Raman spectrum of RDX burning in 10 psi of helium. Laser excitation is  $683\text{ nm}$ .

Raman spectra from  $532\text{ nm}$  excitation. Upon completion of the experiments with  $683\text{ nm}$  excitation, it was decided to revisit the  $532\text{ nm}$  excitation experiments. The reason for abandoning this approach previously hinged on the results of the temperature calibration experiments. The data for temperature calibration at  $532\text{ nm}$  were analyzed again, this time using the more localized background subtraction procedure described above. The results are shown in Figure 3. The agreement over the temperature range of the data is excellent. The prior method of background subtraction had introduced a systematic error at elevated temperature.

Resolution of the temperature calibration allowed the next step of the experiment to investigate the Raman spectrum from the surface of burning RDX at low pressure. The RDX sample was preheated to  $100^\circ\text{C}$  and combusted in a 10 psi helium background. The spectrum was accumulated over 20 seconds (200 laser shots) and transformed by means of the gain calibration to produce the result in Figure 4. The unrejected scatter at  $532\text{ nm}$  and the Raman notch region of the filter ( $0 \pm 500\text{ cm}^{-1}$  shift) have been manually removed from the spectrum while the



**Figure 3.** Temperature calibration of the  $888\text{ cm}^{-1}$  mode of the Raman spectrum of RDX, laser excitation at 532 nm.



**Figure 4.** Raman spectrum of RDX burning in 10 psi of helium. Laser excitation is 532 nm.

background interference is retained to show its predominance in the spectrum. Several Stokes and anti-Stokes modes are readily visible. The feature at  $1850\text{ cm}^{-1}$  is not a recognized transition in the Raman spectrum of RDX and the anti-Stokes range does not extend far enough to determine if it has an anti-Stokes counterpart. The modes at  $602$  and  $888\text{ cm}^{-1}$  were selected for thermometry analysis and the results are indicated in Table 1. Other modes are evident in Fig. 4 however the Stokes modes between  $1000$  and  $1500\text{ cm}^{-1}$  are not resolved well enough to isolate their intensities.

**Table 1.** Results of Raman thermometry from RDX combustion at 10 psi helium pressure.

Raman Mode (cm-1)	anti-Stokes/Stokes Ratio	Temperature (K)
602	0.298	589
888	0.176	601

Discussion of results. The alternate technology for surface temperature measurements is microthermocouples. These devices are typically 3-10 microns in diameter and difficult to fabricate. They are imbedded in the solid and measure the combustion wave as the propellant burns past their position. Thus they provide only one measurement of the surface temperature for each propellant burn. They provide better spatial resolution (10-20 microns) than the current optical technique (200-300 microns), but do not have the sensitivity to chemical species provided by Raman scattering. Several researchers have used the technique and their results are compared with the current measurement in Table 2. The Raman thermometry compares very well with all the microthermocouple results but, most favorably with the work of Zenin, 1995. Zenin's work was the most complete, covering other propellants and pressures up to 90 atmospheres, together with heat transfer analyses that unified the measurements of surface temperature, heat feedback from the gas phase and heat release in the solid phase.

**Table 2.** Comparison of surface temperature measurements.

Surface Temperature* (K)	Diagnostic Technique	Reference
589-601	Raman thermometry	This work
600-610	Microthermocouple	Parr and Hanson-Parr, 1995, 1996
593	Microthermocouple	Zenin, A., 1995
600-635	Microthermocouple	Lu, Y. C., 1996 (Penn State)
* RDX, 1 atmosphere combustion		

Experiments at elevated pressure. The success of Raman thermometry occurred late in the program but the remaining resources were devoted to attempts at surface thermometry at elevated pressure. One remaining sample of RDX was combusted in 10 atmospheres of helium but was consumed so rapidly no Raman spectra were acquired. One small sample of XM39 remained in our inventory from previous studies under ARO funding. This sample was used to obtain calibration spectra in anticipation of successful combustion at 10 atmospheres. The calibration spectra contained a lower level of fluorescence than the spectra from pure RDX but the averaged spectrum from combustion contained low temperature features indicative of the accumulation of Raman signatures before combustion was initiated. The other formulation in our inventory that contained RDX was XM43. Unfortunately this produced spectra during calibration tests and combustion that were completely dominated by fluorescent interference, rendering them unusable for Raman thermometry.

Task II: Two students (Julian Laxton and Eric Boyer) and a Postdoctoral Associate (Y. C. LU) from The Pennsylvania State University were employed during the summers of 1995, 1996, and 1997.

Task III: Comparison of the data to results of other researchers in the field was discussed under the technical accomplishments of Task I. In addition to the papers and reports already disseminated to the solid propellant community, it is anticipated that the results from the final year of this contract will be published in an archival journal.

## CONCLUSIONS

Raman thermometry was shown to be an effective, non intrusive diagnostic for surface temperature measurements of RDX combustion. The temperature sensitivity of the Raman spectrum of RDX was analytically modeled and verified by experimental data. The optical properties, reflectivity and absorptivity, were measured at 532 nm during this investigation. Signal interferences and laser perturbations (laser damage threshold, laser induced heating, laser induced fluorescence) were investigated at excitation wavelengths of 355, 532 and 683 nm. The surface temperature measured with Raman thermometry was in excellent agreement with the results of microthermocouple data obtained in other laboratories. Resources (time and propellant samples) did not allow a full investigation of Raman thermometry at elevated pressure. This investigation provided valuable experience for staff of the URI at The Pennsylvania State University to learn state of the art optical diagnostic techniques in an industrial research environment.

## **PUBLICATIONS AND REPORTS**

Stufflebeam, J. H. (1995). "Surface Diagnostics for Solid Propellant Combustion," Presented at the 32<sup>nd</sup> JANNAF Combustion Meeting, NASA Marshall, Huntsville, AL, 23-27 October.

## **PARTICIPATING SCIENTIFIC PERSONNEL**

John H. Stufflebeam	United Technologies Research Center	(1994-1997)
Julian Laxton	Pennsylvania State University	(1995)
Yeung C. Lu	Pennsylvania State University	(1996)
J. Eric Boyer	Pennsylvania State University	(1997)

## **REPORT OF INVENTIONS**

None

## **REFERENCES**

Lu, Y. C., (1996). Private communication.

Parr, T., and Hanson-Parr, D., (1995). "RDX, HMX, and XM39 Self-Deflagration Flame Structure," Presented at the 32<sup>nd</sup> JANNAF Combustion Subcommittee Meeting, NASA Marshall, Huntsville, Alabama, October.

Parr, T., and Hanson-Parr, D., (1996). "Solid Propellant Flame Structure," in *Decomposition, Combustion, and Detonation Chemistry of Energetic Materials*, Ed. by T. B. Brill, T. P. Russell, W. C. Tao and R. B. Wardle, Materials Research Society Symposium Proceedings, Volume 418, Materials Research Society, Pittsburgh, Pennsylvania.

Zenin, Anatoli, (1995). "HMX and RDX: Combustion Mechanism and Influence on Modern Double-Base Propellant Combustion," *AIAA Journal of Propulsion and Power*, Vol. 11, pp. 752-758.



## APPENDIX A

### **Surface Diagnostics for Solid Propellant Combustion**

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Presented at the 32<sup>nd</sup> JANNAF Combustion Subcommittee Meeting  
NASA Marshall Space Flight Center  
Huntsville, Alabama

23-27 October, 1995

## Surface Diagnostics for Solid Propellant Combustion\*

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### ABSTRACT

The surface region is one of the keys to understanding propellant chemistry. Condensed phase reactions release energy and the interface absorbs heat that is radiated and conducted from the flame. The surface provides coupling for the thermal wave into the solid material which enables the early phase changes and decomposition steps of combustion. Surface temperature measurements are used to calculate the energy balance at this boundary. The surface region is heterogeneous and may be composed of nitramine or daughter fragments surrounded by molten or solid binder molecules. Microthermocouples (~5 mm dia.) have been the diagnostic of choice for surface temperature measurements but the data exhibit large uncertainty because of the physical contact with different phases. Of course, they provide no information on chemical species.

This paper addresses the extremely challenging problem of direct, in situ diagnostics of the heterogeneous surface reaction zone of energetic materials combustion. Specifically, the proposed experiments employ an optical diagnostic, Raman scattering, to provide critically-needed species- and temperature-specific information on surface and near-surface reaction zones of modern, nitramine-based propellant formulations. A critical element of this program is the evaluation of interferences and perturbations that may impact the accuracy of measurements. Experiments will be discussed that employ a laboratory-scale, motorized, and servo-controlled, strand burner over a range of pressure from 1 - 20 atm. Broadband Raman scattering from the surface layer will be acquired with a spectrograph detection system and Stokes/anti-Stokes or Stokes/Stokes ratios will be used to provide surface temperature measurements. Species identification will rely on characteristic Raman shifts of molecular transitions observed in the spectra.

### INTRODUCTION

Fundamental information is needed on solid propellant combustion chemistry. The gas phase chemistry has been investigated in detail over the past several years and one of the major outcomes of this research was a conclusion that even more knowledge is required of the surface region of propellant combustion. The area of surface combustion has proven very difficult to address diagnostically. Models of nitramine/binder combustion are given by Lengelle et al.<sup>1</sup> and Laxton et al.<sup>2</sup>. The surface region is composed of condensed phases and is very heterogeneous, containing liquid, solid and even bubbles of gaseous products. The region is referred to as a foam zone. Ideally, temperature and species information is desired and diagnostics that combine both qualities enhance the experimental approach. Measurements that do not perturb the combustion wave or chemistry are preferred. Thermocouples have provided surface temperature data, however, interpretation of the results is difficult, requires

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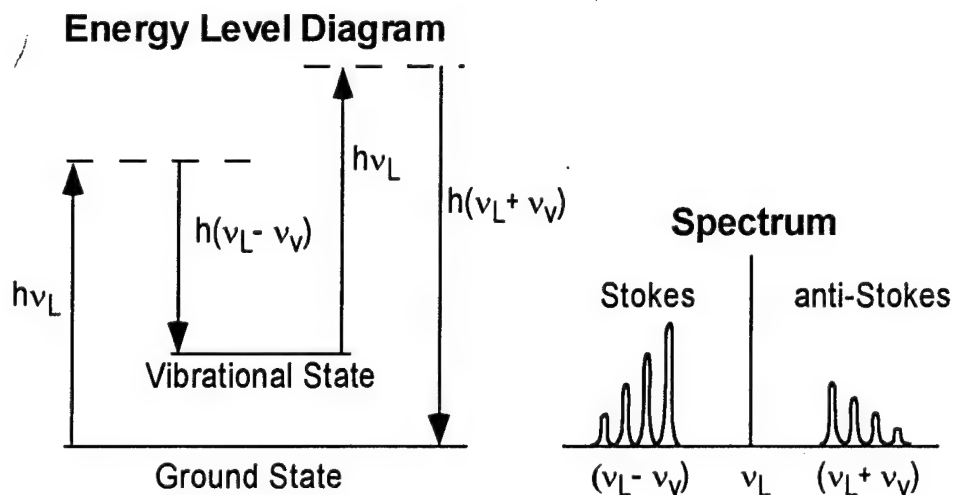
\* Supported by the U.S. Army Research Office, Contract DAAH04-94-C-0076.  
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radiation correction and provides no species sensitivity. Laser diagnostic techniques inherently possess the characteristics required to probe these difficult conditions. Of the laser approaches, Raman scattering, appears to be the best approach to temperature and species measurements of the condensed phases at the surface of burning solid propellants.

The next section briefly reviews Raman scattering and discusses concerns for its specific application in the propellant combustion environment, particularly the nitramine, RDX. The remaining sections address the concerns objectively and present experimental data that will be used to guide an experimental design. An experimental configuration is then presented that will achieve the desired measurements from burning nitramine propellants over the pressure range of 1 - 20 atm. The final sections describe the remaining goals of this three year project, summarize the results to date and, acknowledge the many contributions from colleagues in the solid propellant combustion community.

### RAMAN SIGNAL STRENGTH

Raman scattering is an inelastic optical process<sup>3</sup>; the signal is frequency shifted from the incident radiation by a normal mode (vibrational-rotational) quanta of energy as the molecule makes the transition from its initial to final state. An energy level diagram and the resulting spectrum are illustrated in Fig. 1. A molecule in the ground state interacts with the laser photon and is promoted to the vibrational state. The radiation field loses the quanta associated with the vibrational energy resulting in a frequency shift to longer wavelength, termed Stokes scattering. When the molecule is initially in a vibrational state, the Raman effect returns it to the ground state and produces a photon that has higher energy (lower wavelength). This process is termed anti-Stokes scattering.



**Figure 1.** Raman scattering process and spectrum.

Polyatomic molecules such as RDX have several Raman modes that produce a rich spectrum with many transitions. The anti-Stokes transitions are initiated from a vibrational state which has lower population than the ground state as dictated by the Boltzmann distribution. This implies the anti-Stokes spectrum will be less intense than the Stokes and at room temperature is very difficult to detect. At elevated temperature however the vibrational populations can increase rapidly producing a sensitive tool for temperature measurement.

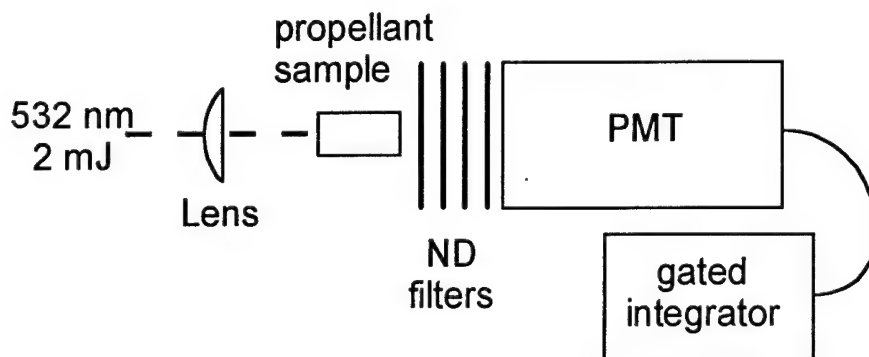
The Raman signal can be calculated from the following equation. The model includes absorptivity and reflectivity because the anticipated application is to condensed phase media.

$$C_0 = \int_0^L P_i (1 - R) e^{-2\alpha z} dz \cdot n_0 \cdot \frac{d\sigma}{d\Omega} \cdot \Omega \cdot \epsilon \quad (1)$$

The signal is represented by  $C_0$ , the number of counts produced at the detector. The integral represents the number of laser photons present at a depth,  $z$ , along the propagation path of the laser. The incident intensity,  $P_i$ , is reduced by the reflectivity,  $R$ , of the material and is attenuated by the absorptivity  $\alpha$ , as it penetrates the medium. The efficiency of the Raman process is characterized by the cross-section  $d\sigma/d\Omega$ ,  $n_0$  is the molecular density of scatterers,  $\Omega$  is the collection solid angle and,  $\epsilon$  represents the efficiency of the detection process. The integral is evaluated over the length of the sample,  $L$ . Absorption of the escaping Raman scattered light is accounted for by the factor of 2 in the exponent of  $e$ . The detection efficiency is accurately determined by laboratory calibration with a tungsten lamp which produces a known spectrum characterized by the filament temperature. The molecular density and collection angle are known and the Raman cross-section is estimated from data of molecules with similar atomic configuration. The optical properties of the medium,  $\alpha$  and  $R$ , are the only remaining unknowns and obviously are very important parameters to measure.

### RDX ABSORPTION

The importance of the absorptivity and reflectivity were exposed in the preceding discussion. In addition to completing the model for signal strength, these parameters impact relevant experimental considerations including laser heating, ablation and, spatial resolution. They have been investigated in the uv region<sup>4</sup> of the spectrum and the IR, however data is lacking for the visible wavelengths, particularly at 532 nm, the second harmonic of Nd:YAG and a potential excitation wavelength for the Raman scattering diagnostic. An experiment was necessary to determine the optical constants at 532 nm and for the morphology of propellant strands, namely, pressed RDX powder. The experiment is depicted in Fig. 2.

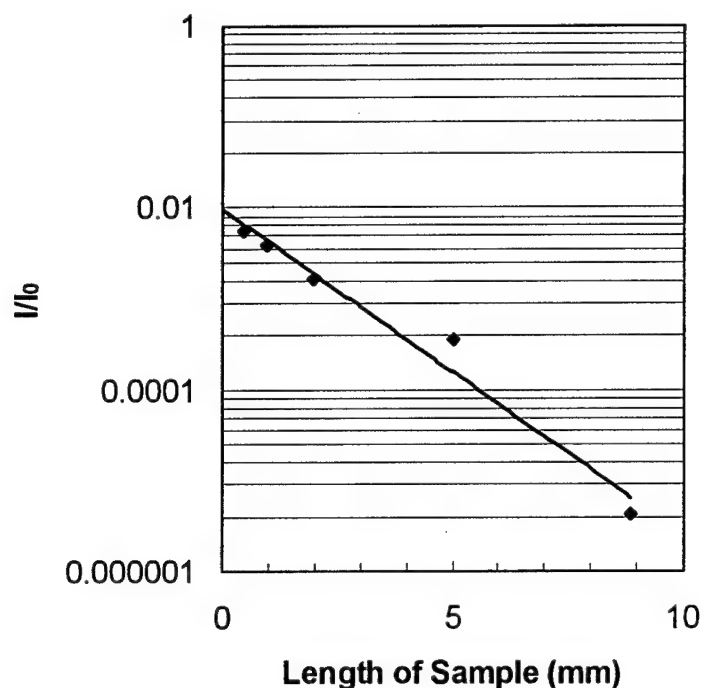


**Figure 2.** Apparatus for the determination of absorptivity and reflectivity of RDX.

The propellant sample is located behind the focus of a 400 mm focal length lens. The lens confines the laser radiation to a spot size of 1 mm at the sample. The configuration is modeled by the following formula,

$$\frac{I}{I_0} = (1 - R) \cdot e^{-\alpha L}$$

$I_0$  is the laser intensity with no propellant sample in the path,  $I$  is measured with the sample in place. Neutral density filters are inserted for each measurement such that the output of the PMT (kept at constant gain) is linear and the reading of the gated integrator is on scale.  $I/I_0$  is evaluated for several samples which have different lengths,  $L$ . The accumulated measurements are plotted on a logarithmic scale and the functional dependence of the formula is used for a regression fit. The results are presented in Fig. 3.



**Figure 3.** Data to determine absorptivity and reflectivity of RDX pressed-powder samples.

With the data presented in this format, the analysis is straightforward; the slope of the regression fit is the absorptivity, 8.2 cm<sup>-1</sup> and, the reflectivity is determined by extrapolation to zero length, 99%. This is a very high reflectivity and a moderate absorptivity. This outcome will allay fears of laser perturbation through heating of the sample, but raise concerns for the spatial resolution that may be achieved in the application to burning propellant strands.

#### POTENTIAL EXPERIMENT PERTURBATIONS

The laser is very energetic and has the potential to perturb the propellant sample. Any laser energy absorbed by the sample will cause heating and the high power of the Q-switched Nd:YAG is capable of ablation of the surface. Photochemistry is another possibility depending on the laser excitation wavelength used. UV wavelengths have a higher probability of causing photochemical effects because there are molecular transitions of RDX that have high absorptivity in the region of 200-350 nm. The low absorption and high reflectivity at 532 nm mitigate concerns of photochemical effects but heating and ablation need further examination.

## LASER HEATING

The previous data that determined the absorptivity and reflectivity of RDX at 532 nm allow a prediction of laser heating. The absorbed laser energy ( $E_0$ ) is converted to heat with an exponential distribution within the sample.

$$Q(x) = E_0 \cdot (1 - R) \cdot e^{-\alpha x}$$

Temperature is calculated from the definition of heat capacity,  $c$ . The density of RDX is  $\rho$ ,  $A$  is the area defined by the diameter of the laser spot and  $x$  is the depth of penetration.

$$T(x) = \frac{\Delta Q}{\rho \cdot (A \cdot \Delta x) \cdot c} = \frac{1}{\rho \cdot A \cdot c} \frac{dQ}{dx}$$

The surface temperature is evaluated from  $T(x)$  in the limit as  $x \rightarrow 0^+$ .

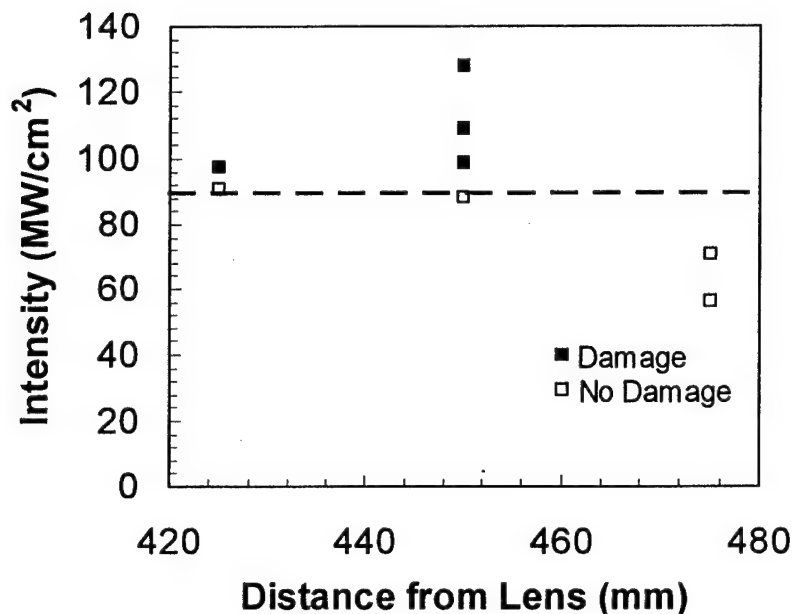
$$T_{\text{surface}} = \frac{E_0 \cdot (1 - R) \cdot \alpha}{\rho \cdot A \cdot c}$$

The predicted surface temperature rise is only 0.05K and thus not a concern for perturbation of chemical reaction rates.

## LASER ABLATION OF RDX PELLETS

Laser ablation is caused by intense laser radiation that may heat the sample, causing a rapid change in to the gas phase and subsequent expansion that ejects material from the surface. An additional mechanism is the extremely high electric field of the laser that can dissociate molecules and expel them from the medium. The first mechanism is not likely, based on the measured absorptivity and reflectivity. The second mechanism is easily evaluated by an experiment that uses some of the apparatus of Fig. 2. Ablation is determined by inspection of the propellant surface after exposure to several thousand laser pulses of controlled intensity. The sample is located at various distances from the lens to control the spot size and the laser energy is varied at that location to control the intensity. The sample is then removed and examined under a microscope for evidence of damage such as pitting. This technique is very sensitive, a pit that is 100 microns in diameter and 10 microns deep is easily noticed, yet represents a weight loss of only  $10^{-7}$  grams. Results are presented in Fig. 4.





**Figure 4.** Data of laser ablation in RDX samples from 532 nm radiation.

The data clearly indicate a damage threshold of 90 MW/cm<sup>2</sup>. This information is important for linear response of the Raman signal as noted later in the paper, as well as the mechanical perturbation of the RDX strand.

#### SIGNAL INTERFERENCES

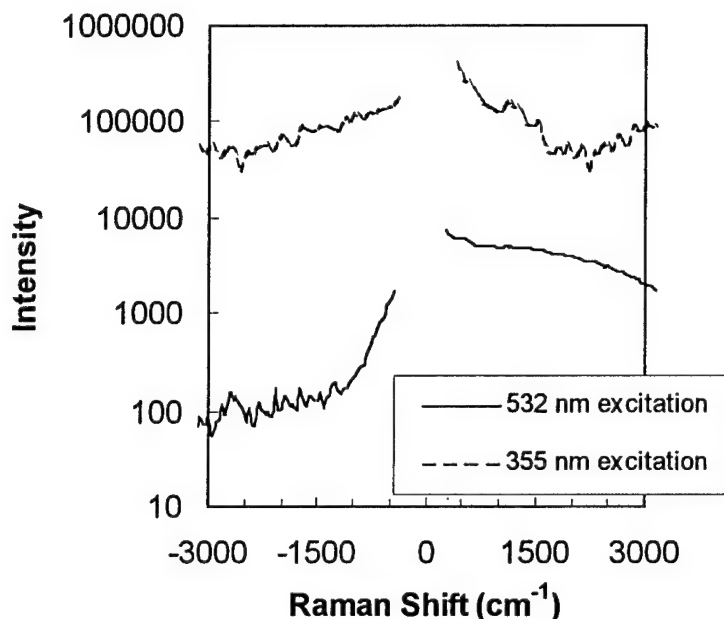
Potential interferences with the Raman signal are laser induced fluorescence and incandescence.

#### INCANDESCENCE

Incandescence can arise both from laser heating of the sample and the normal combustion of the propellant. It is broadband and the spectrum is described by Planck's Law. The predicted surface temperature rise of 0.05K is so small that any increase in incandescence will not be detected. The blackbody radiation from the combusting surface is also low because the expected temperature is only ~600K. The amount of radiation at 532 nm from this distribution (peaked at 4.5 microns) is very small and can be effectively discriminated against by gating the detector. The Raman signal is produced only during the laser pulse while the blackbody radiation is continuous. A detector gate width of 100 nsec will discriminate against any incandescence by a factor of 10<sup>7</sup>.

## RDX FLUORESCENCE

Light can interact with matter through many physical processes. Raman scattering is the focus of this work but another possibility is laser induced fluorescence. The fluorescence may be broadband, intense and, thus interfere with the Raman signal. The laser induced fluorescence of RDX was evaluated for the wavelengths 355 and 532 nm, the second and third harmonics of Nd:YAG. An emission scan of a pressed pellet of RDX was acquired from a SPEX fluorimeter and the results presented in Fig. 5.



**Figure 5.** Fluorescence emission scans of RDX at 355 nm and 532 nm.

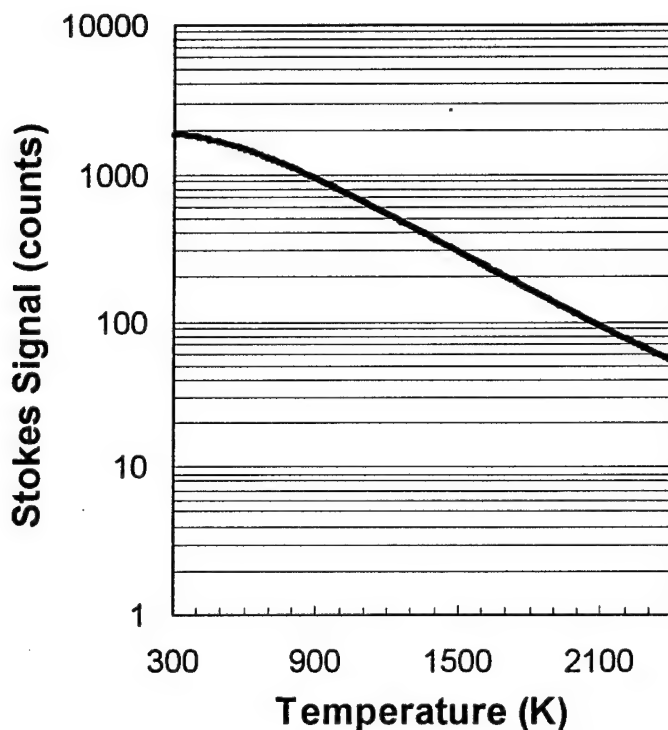
These spectra were recorded over a range of wavelengths that include both the Stokes and anti-Stokes regions of the Raman spectrum for each excitation wavelength. The data indicate that the fluorescence from 355 nm excitation is much higher, by a factor of 20 to 500, than that induced from 532 nm. Therefore to minimize interference from laser induced fluorescence, the Raman scattering should be acquired from 532 nm excitation. This choice is also consistent with minimizing potential photochemical interactions as discussed earlier.

## **RAMAN SCATTERING FROM RDX**

The previous experiments and data have evaluated the Raman scattering approach and addressed technical issues of its application in the environment expected in solid propellant combustion. The data allow quantitative comparisons of the analytical model with experimental results. Of primary importance is the signal intensity.

### RAMAN SIGNAL INTENSITY CALCULATION

Equation 1 can now be evaluated to produce an expectation of the signal level acquired from a Raman scattering experiment with RDX. The calculation is carried out over the temperature range from 300 to 2400K and presented in Fig. 6.

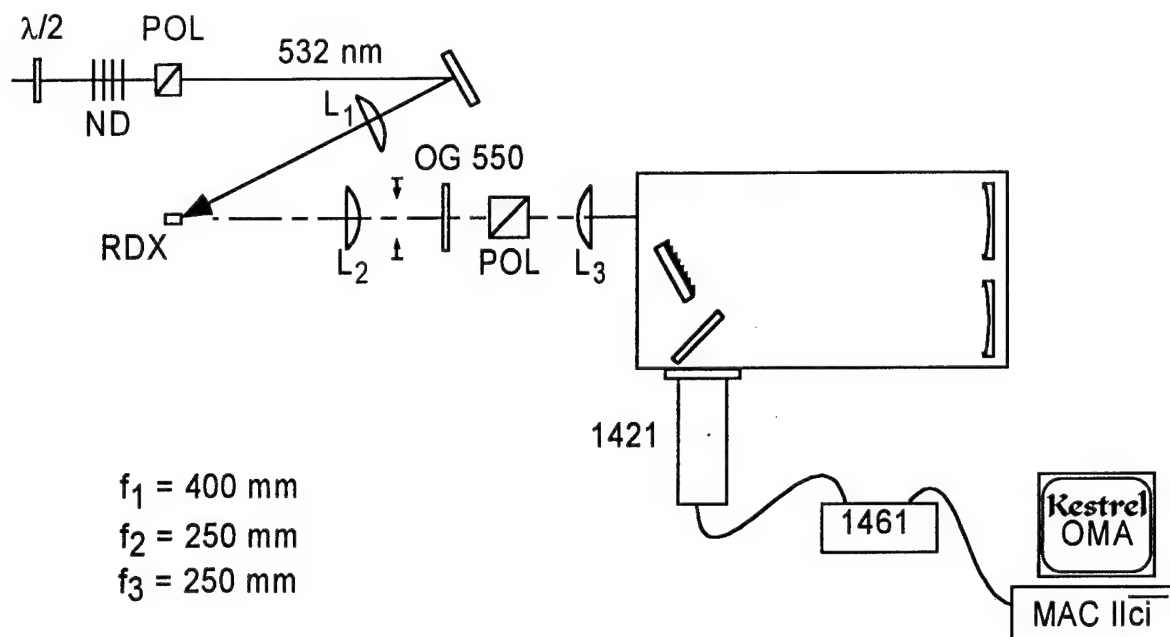


**Figure 6.** Evaluation of Eq. 1 for a laser energy of 1.4 mJ, absorptivity of 8.2 cm<sup>-1</sup> and R=99%.

The model predicts 1860 counts will be detected at room temperature. This is adequate signal to proceed with application of the technique.

### RAMAN SCATTERING EXPERIMENTS

The next step is to compare the Raman scattering model to experimental data from pressed pellets of RDX. Validation of many aspects of the Raman diagnostic configuration can be carried out at room temperature to further insure success in the actual combustion environment. The experimental configuration of Fig. 7 was used to obtain quantitative data from the Raman spectrum of RDX samples..

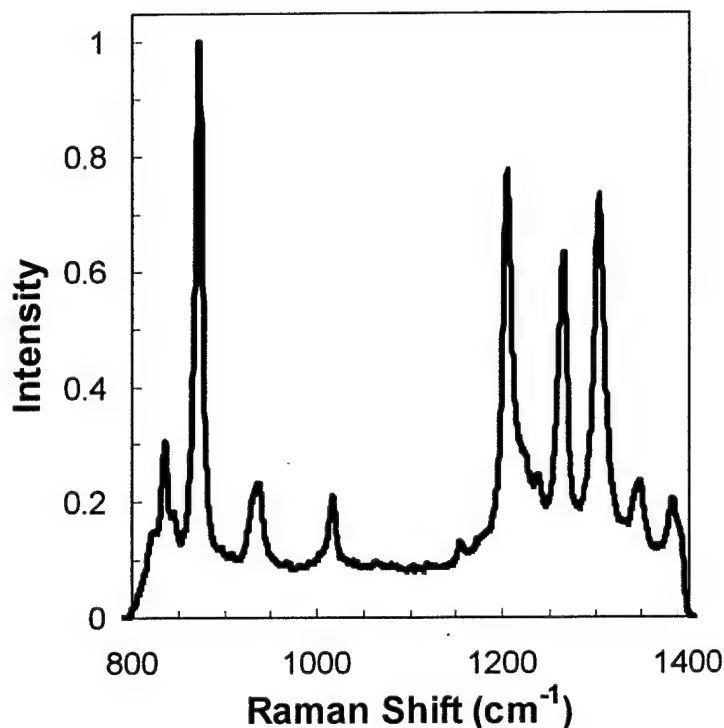


**Figure 7.** Experimental configuration for the acquisition of Raman spectra from solid propellants.

The doubled output (532 nm) of a Q-switched Nd:YAG laser was attenuated to 1.4 mJ/pulse and focused to a 600 micron spot size on the surface of the room temperature propellant. A half-wave plate and polarizer were used to configure the scattering geometry for S-polarization (E-field of the laser is perpendicular to the plane of incidence). The angle of incidence was 45°. The Raman/scattered light was collected with a pair of f/5.8 lenses and focused on the slit of a 0.6 m spectrograph. Schott glass (OG550) was used to absorb any 532 nm radiation collected with the signal. The spectrum was acquired with an intensified photodiode array camera that was controlled by a laboratory computer. The computer also stores the spectra and runs the software for display and analysis of the data.

### RAMAN SPECTRUM OF RDX

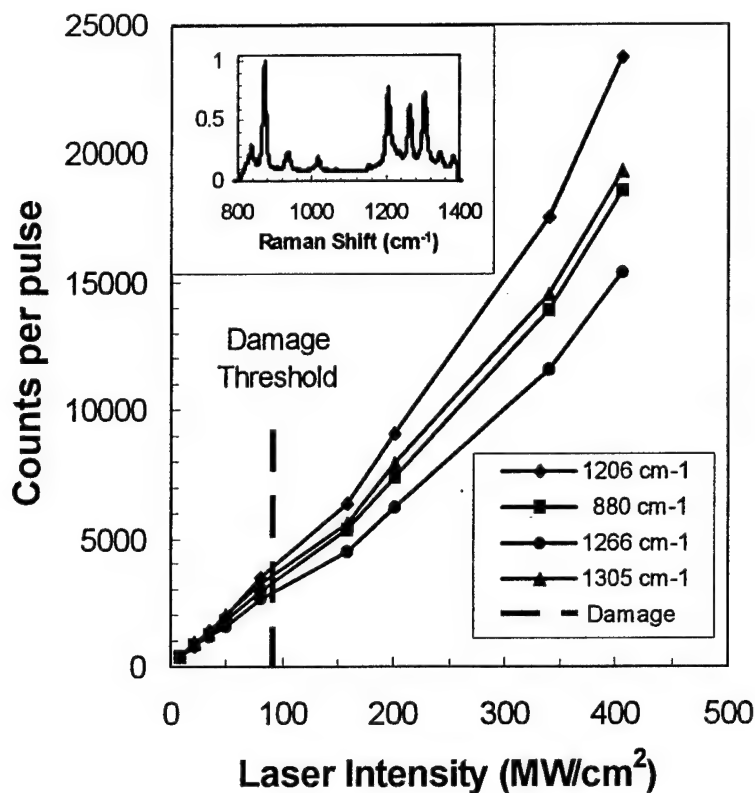
Figure 8 is a spectrum accumulated from twenty, 10 nsec laser pulses. The spectrum registers the Stokes transitions in the range from 800 - 1400  $\text{cm}^{-1}$  shift. The strongest modes are 880  $\text{cm}^{-1}$ , 1206  $\text{cm}^{-1}$ , 1266  $\text{cm}^{-1}$  and 1305  $\text{cm}^{-1}$ . Also evident is the broadband fluorescence that is expected from the data of Fig. 5. It is less than 10% of the Raman signal and can be tolerated, however it could be much more troublesome if the excitation were 355 nm where the laser induced fluorescence is at least 20 times more intense.



**Figure 8.** Raman spectrum from the surface of RDX at room temperature, 532 nm excitation.

#### INTENSITY COMPARISON AND LINEARITY OF RAMAN SIGNAL

Equation 1 predicts a linear relation between the laser excitation  $P_i$  and the signal  $C_o$ . The intensity and linearity of the signal obtained from RDX were tested experimentally by acquiring several spectra with laser energy ranging from 0.25 to 11.5 mJ. The signal detected in the four most intense Raman modes is presented in Fig. 9. The signal detected at 49.5 MW/cm<sup>2</sup> (1.4 mJ/600 micron spot size) is 1975 counts. The analytical model predicted 1860 counts for this condition. The agreement is very good. The data in Fig. 9 clearly show that the signal departs from linearity when the laser damage threshold of 90 MW/cm<sup>2</sup> is exceeded. The mechanism responsible for this behavior is unknown and further elucidation is outside the immediate focus of this project. The data verifies that the diagnostic system must maintain an incident laser intensity less than the damage threshold to yield valid Raman scattering measurements.



**Figure 9.** Detector signal vs. incident laser intensity for the four most intense Raman modes of RDX. Laser damage threshold from Fig. 4 is shown for reference. Inset is the Raman spectrum.

### TEMPERATURE DEPENDENCE OF RDX RAMAN MODES

One goal of this work is the measurement of temperature from the condensed phase of RDX combustion. Raman thermometry can be accomplished by measuring the ratio of anti-Stokes to Stokes intensity. The ratio is given by Long<sup>5</sup>:

$$Ratio = \left( \frac{\nu_L + \nu_i}{\nu_L - \nu_i} \right)^4 \cdot \exp\left( \frac{-h \cdot c \cdot \nu_i}{k \cdot T} \right)$$

Here,  $\nu_L$  and  $\nu_i$  are the laser and vibrational mode frequencies respectively,  $h$  is Planck's constant,  $c$  is the speed of light,  $k$  is the Boltzmann constant and,  $T$  is the temperature. This ratio is plotted in Fig. 10 for several Raman modes. The highest temperature sensitivity is obtained from the modes with the lowest Raman shift. The expected surface temperature is 600-650K, resulting in a ratio of about 20% for the 880 cm<sup>-1</sup> mode.



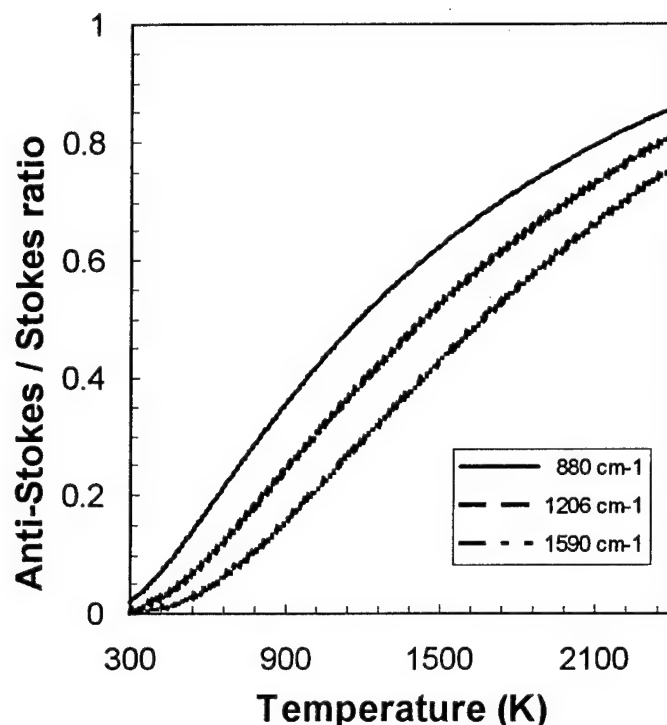
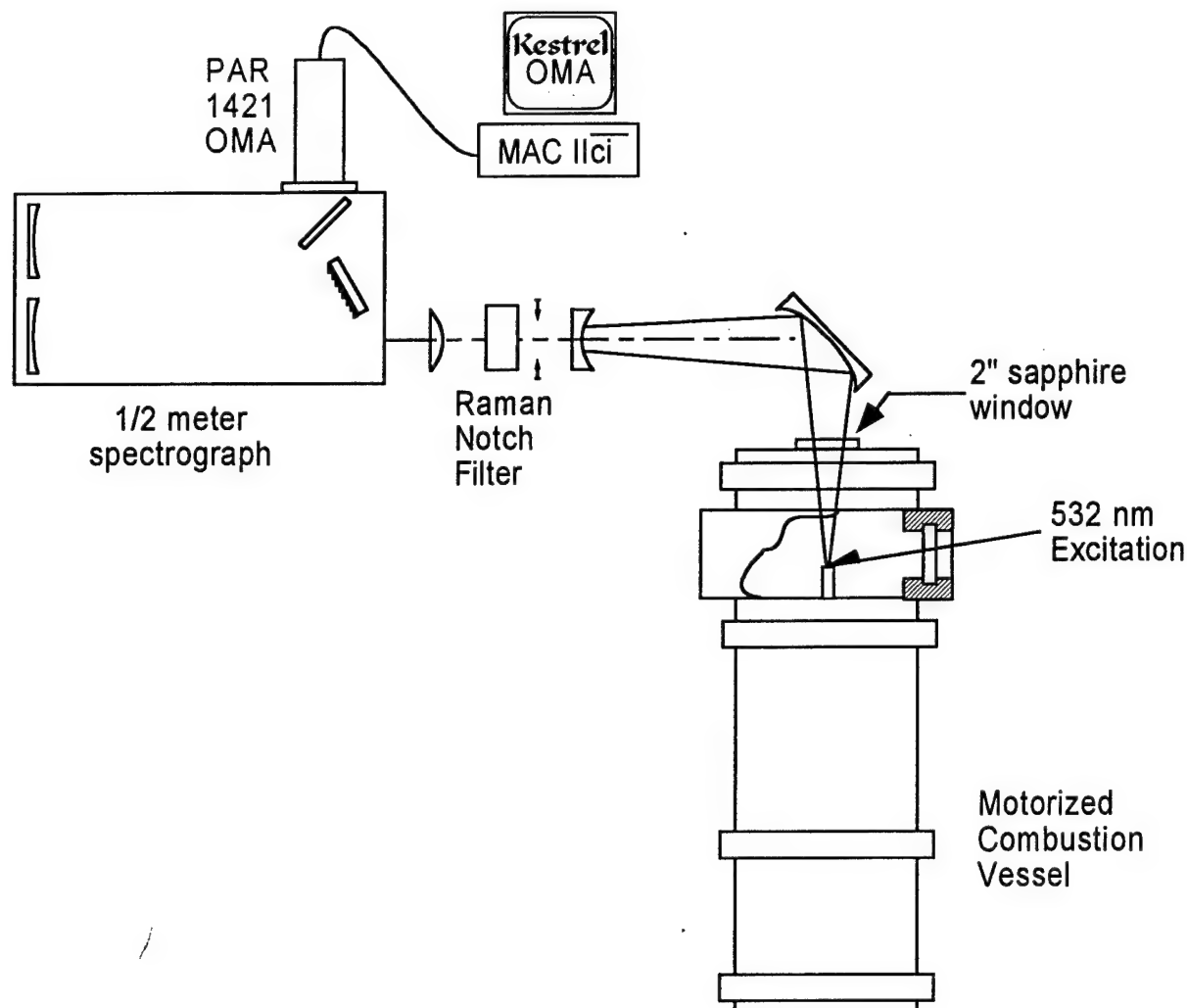


Figure 10. Raman thermometry for RDX surface temperature.

#### EXPERIMENTAL CONFIGURATION FOR SOLID PROPELLANT COMBUSTION

The experiments reported herein now allow the designation of a suitable experimental configuration for Raman thermometry of combusting strands of RDX. The configuration is shown schematically in Fig. 11. A motorized combustion vessel<sup>6</sup> is employed and the 532 nm laser excitation beam is incident at a low angle to the surface. The low angle of incidence will define the vertical spatial resolution, a primary concern of this work. The spatial resolution will be limited to approximately 1/2 the laser beam focal diameter or, 200-300 microns. The horizontal resolution on the planar surface of the propellant is determined by the spectrograph aperture and magnification of the collection optics in this configuration. Typical resolution is 300-500 microns on the surface. Experience with this configuration will allow even lower resolution, both vertical and on the surface, if the signal level is adequate. The Raman scattered radiation is collected through a sapphire window in the top of the chamber and directed to the focusing optics that match the etendu of the spectrograph. A Raman notch filter is used for rejection of any 532 nm radiation in the collection aperture. The notch filter also enables the use of a 1/4 meter spectrograph that is capable of capturing both the Stokes and anti-Stokes transitions in a single spectrum. This will facilitate temperature measurements by the ratioing technique described earlier. The detector and data acquisition system remain the same as previously described.



**Figure 11.** Experimental arrangement for surface Raman scattering from burning propellants.

#### FUTURE WORK

The program for Raman Surface Diagnostics of Solid Propellant Combustion is a three year project with one year completed. The remaining goals are to calibrate the Raman temperature dependence by utilizing the internal heater (oven) in the solid propellant combustion vessel to preheat the samples to the desired temperature before acquiring the spectrum. The heating technique can be used to produce liquid phase RDX in the combustion vessel and investigate its spectrum. This experiment has the potential to provide a liquid./solid discriminator via the reported<sup>7</sup> shift of the C-H modes of RDX during the phase transition. The magnitude of the shift ( $37\text{ cm}^{-1}$ ) is well within the experimental resolution of the UTRC apparatus. The program will then proceed to acquire Raman Spectra from burning RDX at pressures over the range of 1-20 atm. Data analysis will provide surface temperature measurements and the spectra will be evaluated for additional molecular signatures which may be present.

## SUMMARY

The application of Raman scattering has been shown to be a viable approach to surface diagnostics of solid propellant combustion. The technical concerns have been discussed including signal/noise ratio, potential laser perturbations and, temperature sensitivity. The signal level was experimentally shown to be adequate and compared favorably with the model predictions. Laser perturbations and interferences were shown to be avoidable by proper selection of experimental parameters. The data acquired to date allowed the design of an apparatus to obtain Raman spectra from the surface of burning propellants and future steps toward that goal were outlined.

## ACKNOWLEDGEMENTS

The author wishes to acknowledge the many helpful contributions from colleagues in the solid propellant combustion community. Dr. Timothy Parr of the Naval Air Warfare Center at China Lake, CA has graciously provided the pressed-powder RDX samples used in this work, along with helpful advice on diagnostics of their combustion. Julian Laxton, a graduate student at The Pennsylvania State University performed the ablation and fluorescence measurements during a summer internship at UTRC. Drs. Alan Eckbreth and Michael Winter of UTRC have provided many useful discussions and program guidance.

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## **APPENDIX B**

### **Surface and Gas-Phase Diagnostics for Solid Propellant Combustion**

*John H. Stufflebeam  
United Technologies Research Center  
East Hartford, CT 06108*

Interim Progress Report  
ARO Contract DAAH04-94-C-0076  
January 1 - December 31, 1996

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE		3. REPORT TYPE AND DATES COVERED Interim Report, 01 Jan 96 - 31 Dec 96
4. TITLE AND SUBTITLE Surface and Gas-Phase Diagnostics for Solid Propellant Combustion			5. FUNDING NUMBERS  C: DAAH04-94-C-0076	
6. AUTHOR(S)  John H. Stufflebeam				
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13. ABSTRACT (Maximum 200 words)  This program addresses the extremely challenging problem of direct, in situ diagnostics of the heterogeneous surface reaction zone of energetic materials combustion. Specifically, the experiments employ an optical diagnostic, Raman scattering, to provide critically-needed species- and temperature-specific information on surface and near-surface reaction zones of nitramine-based propellant formulations. During this reporting period experiments were performed to calibrate the temperature sensitivity of the Raman spectrum of RDX. Stokes and anti-Stokes signatures were also acquired from the surface of a combusting pellet of RDX. The signal to noise ratio of the Raman spectrum deteriorated rapidly as the temperature increased above 100°C. The results indicate a change of excitation wavelength is necessary, longer wavelength excitation should decrease the fluorescence interference. Implementation of the design during the coming year will employ a Raman sift cell to produce 683 nm excitation from the first Stokes mode of hydrogen when pumped by the 532 nm from a Nd:YAG. Broadband Raman scattering from the surface layer will be acquired with a spectrograph detection system and Stokes/anti-Stokes or Stokes/Stokes ratios will be used to provide surface temperature measurements.				
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None

**(2) SCIENTIFIC PERSONNEL supported by this project:**

John H. Stufflebeam (UTRC)  
Yeung C. Lu (The Pennsylvania State University)

**HONORS/AWARDS/DEGREES received during this reporting period:**

None

**(3) Report of INVENTIONS (By TITLE ONLY):**

None

**(4) SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS:**

The application of Raman scattering is a viable approach to surface diagnostics of solid propellant combustion. The technical concerns include signal/noise ratio, spatial resolution on the order of 100  $\mu\text{m}$  (to limit averaging over the steep temperature gradient), potential laser perturbations and, temperature sensitivity. The signal/noise ratio of the room temperature Raman spectrum of RDX was shown to be adequate (Fig. 1), however the signal/noise ratio deteriorated as the temperature increased. A change in excitation wavelength is necessary to reduce the fluorescence intensity. The data acquired to date allow the design of an apparatus to obtain Raman spectra from the surface of burning propellants. During the next reporting period, the design will be implemented and produce Raman data for surface temperature measurements.

Signal to Noise Ratio of the Raman Spectrum of RDX Excited at 532 nm. Laboratory experiments confirmed adequate signal to noise ratio in the Raman spectrum of RDX at room temperature. Figure 1 is a spectrum accumulated from twenty, 10 nsec laser pulses. The spectrum registers the Stokes transitions in the range from 800 - 1400  $\text{cm}^{-1}$  shift. The strongest modes are 888  $\text{cm}^{-1}$ , 1206  $\text{cm}^{-1}$ , 1266  $\text{cm}^{-1}$  and 1305  $\text{cm}^{-1}$ . Also evident is the broadband fluorescence that is expected from the 532 nm excitation. It is less than 10% of the Raman signal and can be tolerated. Previous experiments have shown the fluorescence at 532 nm is 20 times weaker than that produced by 355 nm (the third harmonic of Nd:YAG).

Calibration of the temperature sensitivity of the Raman spectrum of RDX was accomplished by acquiring spectra as the surface of the pellet was heated to various temperatures. The RDX sample was heated by the internal oven of the solid propellant combustion vessel. A thermocouple was fixed to the bottom surface which was in contact with the heating device and also one was attached to the top surface which was



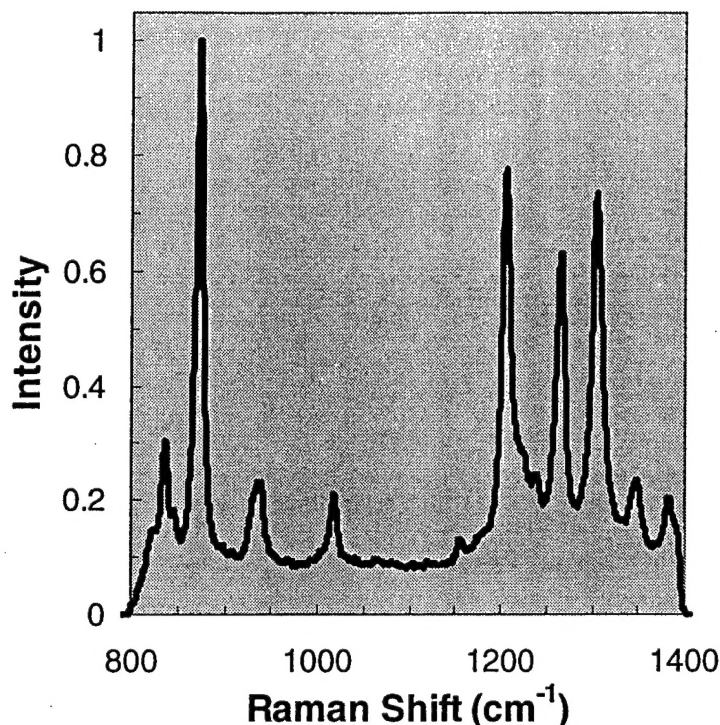


Figure 1. Raman spectrum from the surface of RDX at room temperature, 532 nm excitation.

irradiated with the excitation laser. The bottom thermocouple (at the warmest temperature) was monitored to insure the RDX sample did not exceed the melting point.

The highest temperature achieved on the free surface was 128C. The pellet was slowly heated and equilibrium temperatures were reached before acquisition of the spectrum. Shown in Fig. 2 are six spectra that are representative of the sampled temperature range. The spectra have been corrected for the gain of the detection system by using a tungsten lamp whose filament temperature was measured with an optical pyrometer. Both the Stokes and anti-Stokes modes are presented in the figure. The lower spectrum is at room temperature and as the temperature is increased, the background interference increases, raising the spectra observed at elevated temperatures. The signal to interference ratio of the anti-Stokes modes decreases from approximately 5:1 to less than 1:1 at the highest temperature. These are lower signal to noise than the Stokes modes but critical for measurement of the surface temperature and thus are cited in this analysis. The background interference seems to saturate at the high temperature, with not much difference in the interference component between the spectra at 111C and 128C. Unfortunately this level of signal to noise is not acceptable for accurate surface temperature measurements.

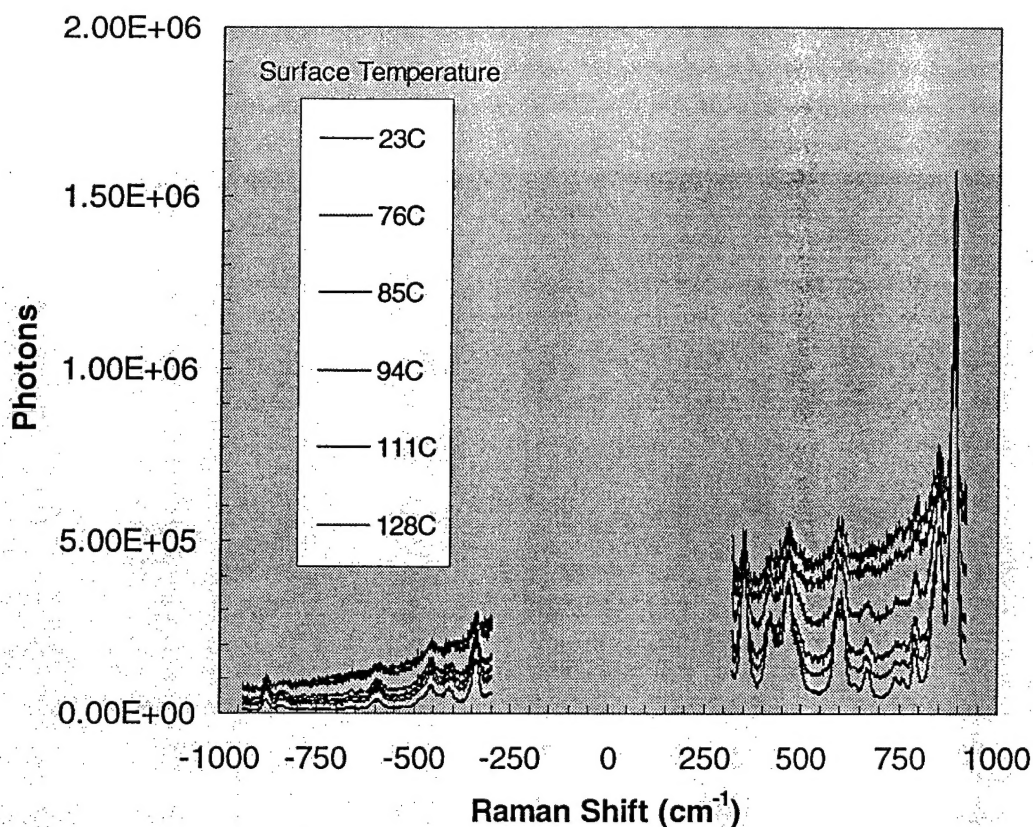


Figure 2/ Temperature sensitivity of the Raman spectrum of RDX. Excitation wavelength is 532 nm.

Comparison of Experiment and Analytical Model. The data of Figure 2 were compared to the analytical model that was developed for surface temperature measurements in the first year of this investigation. The model relies on the ratio of anti-Stokes to Stokes mode intensities. The following figure shows the results for the 888 cm<sup>-1</sup> mode, the model prediction is the black dashed line. The analytical calculation fits the experimental data very well up to 100C, then the data drop off sharply. Although the ratio compares favorably to the model, the mode intensities fall off much more rapidly than expected from the analytical model, i.e. it seems there is a loss of RDX Raman intensity. A literature search does not support evidence of chemical reactions that consume RDX molecules at these low temperatures. A consistent hypothesis is that the optical properties of RDX are changing with increased temperature. Increased reflectivity of the sample would decrease the incident excitation intensity and produce lower Raman signal. Increased absorption would increase the fluorescence intensity consistent with the increase of background interference that is observed. Increased absorption would also decrease the intensity of Raman scattered signal that was propagated out of the sample, again, consistent with observation.

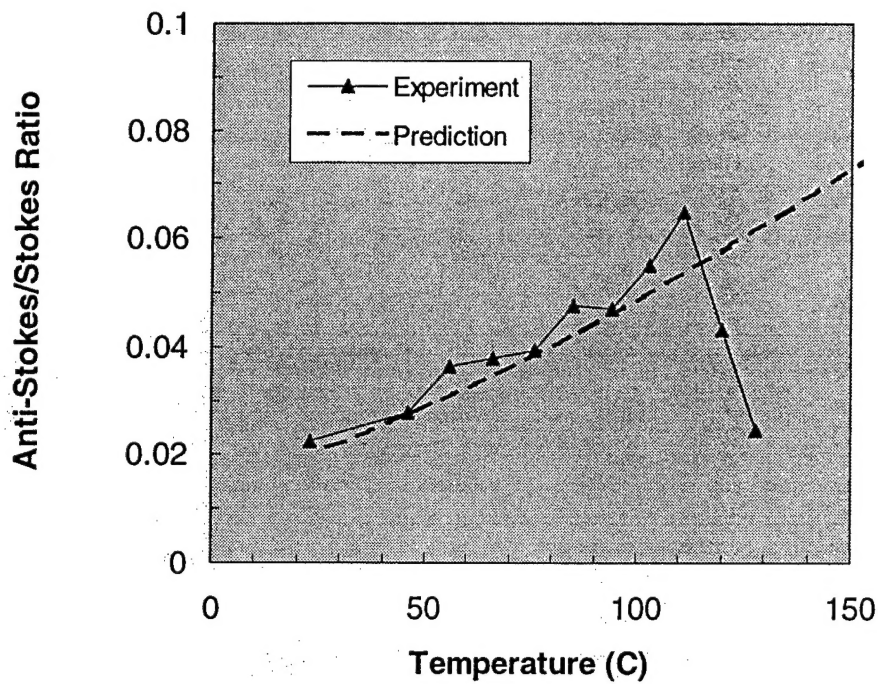


Figure 3. Temperature calibration of RDX Raman spectrum.  $888\text{ cm}^{-1}$  mode,  $532\text{ nm}$  excitation.

A strategy to alleviate the poor signal to noise ratio incorporates an alternate excitation wavelength. Previous data showed increased fluorescence from  $355\text{ nm}$  excitation, and data in the literature support stronger absorption in the uv. Normally, longer wavelengths produce lower fluorescence and absorption.

Optimized Experimental Configuration. The experimental results reported here were used for the designation of a suitable experimental configuration for Raman thermometry of combusting strands of RDX. The configuration is shown schematically in Fig. 4. The  $532\text{ nm}$  radiation from a Nd:YAG laser is propagated through a pressurized hydrogen cell to produce a narrowband, red-shifted excitation source for the RDX experiments. The longer excitation wavelength will produce lower fluorescence interference and improve the signal to noise ratio. The first Stokes mode of hydrogen produces radiation at  $683\text{ nm}$  which is incident at a low angle to the RDX surface inside the motorized combustion vessel. The low angle of incidence will define the vertical spatial resolution, a primary concern of this work. The spatial resolution will be limited to approximately  $1/2$  the laser beam focal diameter or,  $200\text{-}300\text{ microns}$ . The horizontal resolution on the planar surface of the propellant is determined by the spectrograph aperture and magnification of the collection optics in this configuration. Typical resolution is  $300\text{-}500\text{ microns}$  on the surface. Experience with this configuration will allow even lower resolution, both

vertical and on the surface, if the signal level is adequate. The Raman scattered radiation is collected through a sapphire window in the top of the chamber and directed to the focusing optics that match the etendue of the spectrograph. A Raman notch filter is used for rejection of any 683 nm radiation in the collection aperture. The notch filter also enables the use of a 1/4 meter spectrograph that is capable of capturing both the Stokes and anti-Stokes transitions in a single spectrum. This will facilitate temperature measurements by the ratioing technique described earlier. The detector is a 1000-channel, intensified, photodiode array controlled by the Macintosh computer.

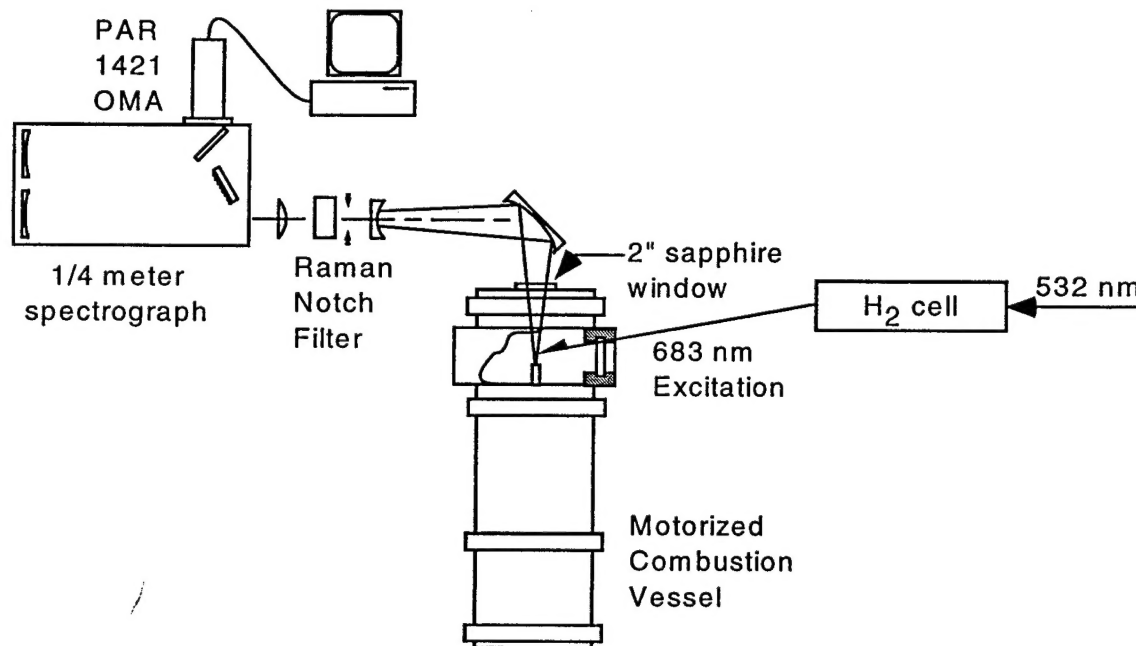


Figure 4. Experimental arrangement for surface Raman scattering from burning propellants.

**(5) TECHNOLOGY TRANSFER:**

None